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Large-scale pesticide monitoring across Great Barrier Reef catchments – Paddock to Reef Integrated Monitoring, Modelling and Reporting Program

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ABSTRACT

The transport and potential toxicity of pesticides in Queensland (QLD) catchments from agricultural areas is a key concern for the Great Barrier Reef (GBR). In 2009, a pesticide monitoring program was established as part of the Australian and QLD Governments' Reef Plan (2009). Samples were collected at eight End of System sites (above the tidal zone) and three sub-catchment sites. At least two pesticides were detected at every site including insecticides, fungicides, herbicides, and the Reef Plan's (2009) five priority photosystem II (PSII) herbicides (diuron, atrazine, hexazinone, tebuthiuron and ametryn). Diuron, atrazine and metolachlor exceeded Australian and New Zealand water quality guideline trigger values (TVs) at eight sites. Accounting for PSII herbicide mixtures increased the estimated toxicity and led to larger exceedances of the TVs at more sites. This study demonstrates the widespread contamination of pesticides, particularly PSII herbicides, across the GBR catchment area which discharges to the GBR.

1. Introduction

The Great Barrier Reef World Heritage Area is not a closed system and therefore activities that occur in regions adjacent to the Great Barrier Reef (GBR) will influence the functioning of the GBR. The importance of maintaining the biodiversity, health and functional plasticity of the GBR is of national and international interest (United Nations Educational, Scientific and Cultural Organisation World Heritage Convention, 1981). Hence it is not surprising that human activities undertaken in these adjacent regions are under scrutiny for their potential impacts to the GBR.

A close relationship of the ecosystems along the Queensland coast exists with the GBR (see Haynes et al., 2007 for a conceptual model). The freshwater riverine systems, wetlands, mangroves and seagrasses support the reef through the provision of fisheries habitats, filtration of terrestrial runoff, nutrient cycling and key components of the foodweb (Costanza et al., 1997; Duke et al., 2005; Schaffelke et al., 2005; Waycott et al., 2007). The importance of the supporting services that these adjacent ecosystems provide has been highlighted by Stoeckl et al.'s (2011) report on the economic value of the GBR. They (Stoeckl et al., 2011) emphasised the critical nature of anthropogenic impacts on the "supporting services", without which, the ability of the reef to provide its services would deteriorate. With the GBR services valued at over AUS$5 billion (Access Economics, 2005), the decline of the adjacent ecosystems becomes not just an environmental issue, but an important economical issue as well.

Poor water quality in GBR catchments is problematic to the GBR in two ways (1) pollutants are transported to the GBR and cause direct impacts to reef biota; and (2) pollutants impact the biota within the freshwater and estuaries of the riverine systems and this affects the services that the river systems provide to the GBR. The poor water quality is principally a result of land clearing and agricultural land-use practices since European settlement that have introduced man-made chemicals (i.e. pesticides) and generated loads of sediment and nutrients above natural levels (Brodie et al., 2008).

Pesticides have been detected in the water (Shaw and Müller, 2005; Davis et al., 2008; Lewis et al., 2009; Packett et al., 2009), sediment (Duke et al., 2005) and biota (Haynes et al., 2000; Mortimer, 2000) of GBR catchments and these include insecticides, herbicides and fungicides (Haynes and Michalek-Wagner, 2000). These contaminants are transported in runoff from paddocks and enter creeks and rivers that feed into the GBR lagoon (Haynes and Michalek-Wagner, 2000). With agriculture occupying approximately 70% of land in the GBR catchment area (GBRCA) (Australian Bureau of Statistics, 2011) including grazing, sugar cane, horticulture, plantation forestry, pasture, cropping and cotton, there is concern that pesticides pose a direct threat to GBR biota. Currently, more than 200 pesticides (i.e. active ingredients) are registered for use with the Australian Pesticides and Veterinary Medicines Authority (Shaw et al., 2011), of which, it is the herbicides that inhibit photosystem II (called PSII herbicides) that have been most

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frequently detected in the GBR lagoon (Shaw and Müller, 2005; Bainbridge et al., 2009; Lewis et al., 2009) and throughout the GBRCA (Davis et al., 2008; Mitchell et al., 2005; Packett et al., 2009).

PSII herbicides act by inhibiting photosynthesis and target a specific group of organisms, phototrophs. In the GBR, PSII herbicides have been detected in seagrasses which are an important food source for dugongs and provide nurseries for reef fish (Haynes et al., 2000). Studies have also proven that PSII herbicides can induce coral bleaching by impacting zooxanthellae (symbiotic dinoflagellates) which leads to their expulsion from the coral (Jones et al., 2003; Negri et al., 2005). In addition, benthic microalgae and crustose coralline algae have been shown to be sensitive to PSII herbicide inhibition (Magnusson et al., 2010; Harrington et al., 2005, respectively).

Pesticides are often found in mixtures, but to date, the potential threat of pesticides to the GBR has only been assessed for individual chemicals. The scientific consensus of water quality in the GBR indicated that the potential interactive effects of pesticide mixtures were a key uncertainty of the causal relationship between water quality and ecosystem health (Brodie et al., 2008). Therefore, assessing the potential impact of pesticides as a mixture is of high importance to ensure the ecological health of the GBR is maintained.

It is well established that chemicals that exhibit the same mode of action conform to the concentration addition model (Mumtaz et al., 1994). PSII herbicides, in combination, have been proven to conform to this model of mixture toxicity and to produce additive toxic effects to exposed organisms (Faust et al., 2001; Magnusson et al., 2010). Ma (2002) generated dose response curves for 30 herbicides including PSII herbicides. Thus, there exists a data set to derive toxic equivalent quotients (TEQs) for determining the toxicity of a mixture of PSII herbicides from the concentrations of the constituents.

In 2009, a large-scale pesticide monitoring program was funded as part of the Queensland Government's commitment to the joint Australian and Queensland Government "Paddock to Reef Integrated Monitoring, Modelling and Reporting Program". This was established in order to measure progress towards the Reef Plan (2009) water quality goals and targets. The pesticide monitoring program was developed as part of a coordinated effort to assess the success of agricultural management strategies in reducing the loads of five priority PSII herbicides (atrazine, diuron, hexazinone, tebuthiuron and ametryn) in riverine systems. This paper reports on the initial findings from the first year (2009/2010) of monitoring for the GBR pesticide monitoring program. The objectives for reporting these initial findings were to: (1) provide a spatial overview of pesticide inputs to the GBR lagoon and end-of-system aquatic habitats associated with GBR catchments; (2) assess the degree of contamination, i.e. the number and types of pesticides, the concentration of pesticides and duration of exposure; and (3) assess the potential toxicity of pesticides occurring as a mixture.

2. Materials and methods

2.1. Study area

The GBRCA is comprised of 35 coastal catchments situated in north-east and central Queensland, Australia, which drain into the GBR lagoon (Fig. 1). Eleven sites were monitored from eight catchments, with eight End of System sites (above the tidal influence) and three sub-catchment sites (Fig. 1) that all represented areas with high agricultural land use. The sites were selected based on a previous hazard assessment (Shaw et al., 2011) which identified these catchments as being the largest potential contributors to pesticide loads entering the GBR and therefore posing the greatest potential risk. The catchments were distributed across five of the six Natural Resource Management (NRM) regions that cover the GBRCA. All catchments drained directly into the GBR lagoon except for Barratta Creek, which drains firstly into Bowling Green Bay, a RAMSAR wetland.

2.2. Grab sampling

Manual grab samples (1 L) were collected at each site over at least two flow events from the 2009/2010 wet season. Samples were collected from approximately 0.3 m below the water surface in an area of high flow, in close proximity to deployed passive samplers. Samples were collected directly into solvent rinsed, 1 L glass bottles, transported on ice and stored in the dark at ~4 °C before analysis. The number of grab samples collected and the timing of collection was based on the occurrence of large flow events at each site. The objective was to sample at least two events such that approximately four samples were collected on the rise of an event and three samples were collected on the fall of an event, but more were collected if possible. This was not always possible at some sites as logistical issues (e.g. flooding) made it impossible to do so. A total of 268 grab samples were collected and chemically analysed across all sites.

All grab water samples were chemically analysed by Queensland Health Forensic and Scientific Services (QHFSS), a National Association of Testing Authorities (NATA) accredited laboratory. Water samples were analysed using a multi-residue method for the determination of organochlorine (OC, neurotoxins) and organophosphorus (OP, cholinesterase inhibitors) pesticides, acetylcholine agonists, synthetic pyrethroids pesticides, triazine herbicides (PSII herbicides) including atrazine, simazine and prometryn, bromacil (PSII herbicide), trifluralin (seedling growth inhibitor), substituted urea herbicides (PSII herbicides) and polychlorinated biphenyls (PCBs). A liquid/liquid extraction was performed on 1 L samples using 250 mL of dichloromethane. The filtered extracts were concentrated under nitrogen gas and low heat. For analysis by liquid chromatography tandem mass spectrometry (LC–MS/MS) only (substituted ureas, triazines, bromacil and imidacloprid), the extract was further prepared by the addition of 5 mL of hexane, followed by a second concentration stage and the addition of methanol.

All samples were analysed by high performance LC–MS/MS using an AB/Sciex API 300 mass spectrometer (Applied Biosystems, Concord, On, Canada) equipped with a heated nebuliser (chemical ionisation) interface coupled to a Shimadzu SCL-10A*vp* HPLC system (Shimadzu Corp., Kyoto, Japan). Selected samples were also analysed by gas chromatography mass spectrometry (GC–MS) for the determination of OC, OP, PCBs, synthetic pyrethroids and triazines. GC–MS analysis was performed on a Shimadzu QP5050A GC–MS.

Analysis of samples for phenoxy acid herbicides (synthetic auxins) was performed separately. Only selected samples from Sandy and Barratta Creeks were tested for phenoxy acid herbicides. Samples were first hydrolysed with sodium hydroxide to convert herbicide esters to the sodium salt form. Samples were then acidified, and the phenoxy acid herbicides were extracted by solid phase extraction using a polymeric cartridge (Oasis HLB, Waters Australia), and 2% NH_4OH/98% acetonitrile followed by dichloromethane solvent eluent. The extract was evaporated just to dryness and prepared in 10% methanol aqueous solution. The phenoxy acid herbicides were then analysed by high performance LC–MS/MS.

2.3. Passive sampling

Passive samplers were deployed at each site throughout the 2009/2010 wet season to measure the presence/absence of

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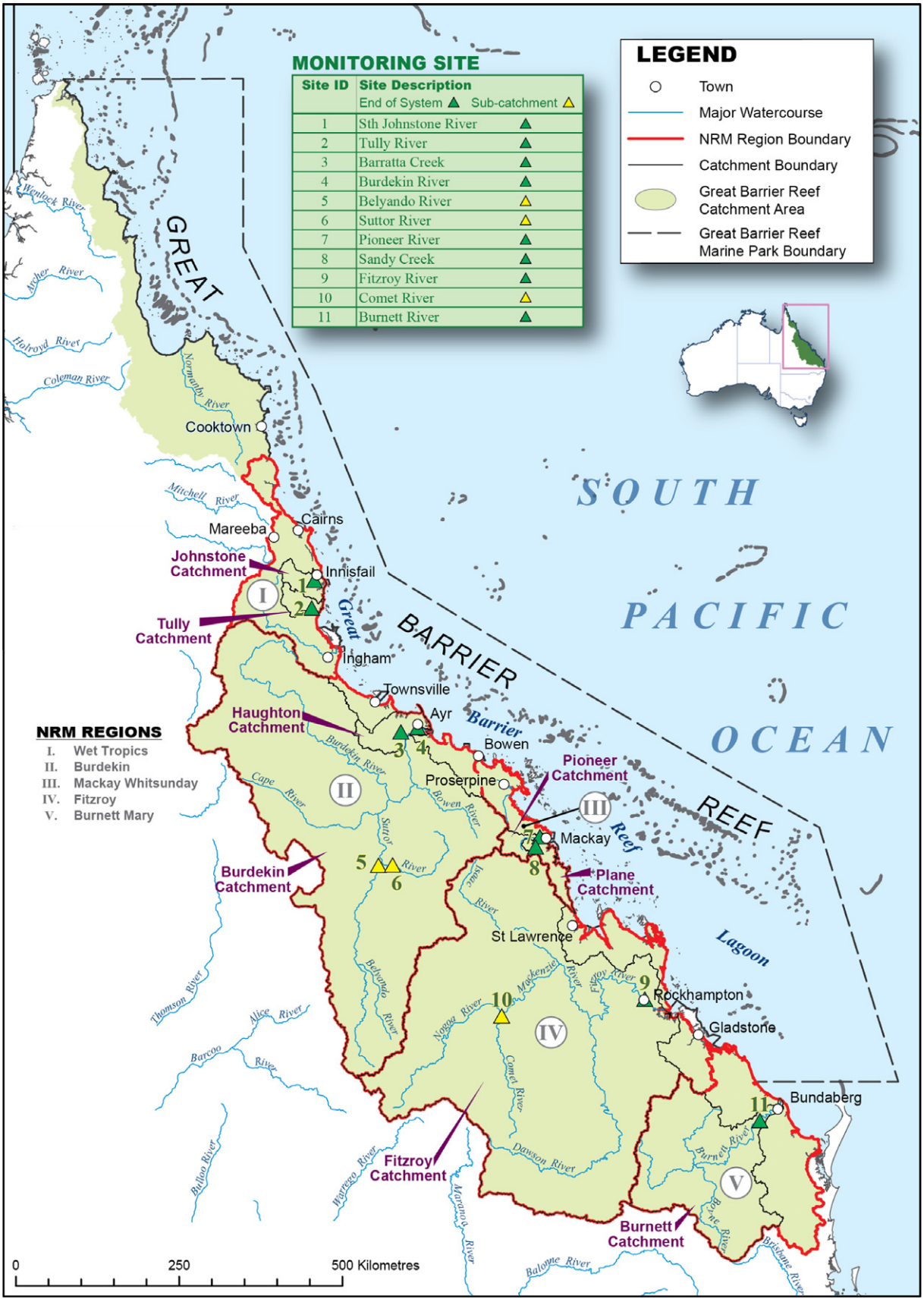

Fig. 1. End of System and sub-catchment pesticide monitoring sites of the Reef Plan (2009) Paddock to Reef Program for the 2009/2010 wet season.

pesticides over extended periods. A passive sampler unit consisted of three types of passive monitors; two SDB–RPS Empore™ disks (EDs), a semipermeable membrane device (SPMD) and a polydimethylsiloxane (PDMS) device. The EDs were mounted in Teflon

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Table 1
EC50 concentrations for *Scenedesmus obliquus* and *Chlorella pyrenoidosa* derived from Ma (2002) and calculated atrazine toxic equivalency factors (TEF).

Species	Units	Atrazine	Diuron	Ametryn	Simazine	Prometryn
Scenedesmus obliquus	EC50 µM	0.573	0.0175	0.0515	1.27	0.0069
	TEF atrazine	1.00	32.74	11.13	0.45	83.04
Chlorella pyrenoidosa	EC50 µM	0.6720	0.00559	0.00141	0.409	0.0493
	TEF atrazine	1.00	120.21	476.60	1.64	13.63

cases that hold the disks in position and allow the membrane to be exposed to the passing flow, as well as protecting the membranes from passing debris. The PDMS and SPMD were mounted in a stainless steel cage that allowed for the surrounding water to move through the cage and come into contact with the membranes.

The passive sampler membranes were prepared by the National Research Centre for Environmental Toxicology (EnTox), using an established method (Shaw et al., 2010). Passive sampler units were deployed in the flow of the stream for up to a month. However, if a large flow event occurred during deployment, the sampling unit was collected as soon as possible once flow had returned to base conditions/levels. Upon retrieval of a passive sampling unit from the field, the passive samplers were transported (on ice) to EnTox for extraction of the aggregated pesticides and analysis. Methods of extraction and analysis have previously been described (Shaw et al., 2010). A total of 50 passive samplers were deployed with 44 of these analysed for pesticide residues. Six passive samplers were lost or damaged during deployment and therefore could not be analysed.

2.4. Flow measurements

The Department of Environment and Resource Management (QLD State Government) gauging stations recorded river height in accordance with Water Resource Plans for the allocation and sustainable management of water as a requirement of the Water Act (2000) (DNRW, 2007). Discharge was then calculated from the river height and the flow velocity based on the cross-sectional area.

2.5. Toxic equivalency quotients

The toxic equivalent quotient (TEQ) was calculated to provide a measure of toxicity for PSII mixtures detected from grab samples. TEQ concentrations were calculated according to Safe (1998) using the following equation:

$$\mathrm{TEQ} = \sum C_i \times \mathrm{TEF}_i$$

where, C_i = the concentration of individual compounds, and TEF = - toxic equivalency factor of the individual compounds.

The TEFs were determined based on the study by Ma (2002), from which EC50 concentrations were calculated for five PSII herbicides: atrazine; diuron; ametryn; simazine; and prometryn (Table 1). Ma (2002) was used to calculate the TEFs as it provided EC50 concentrations from an acute 96 h growth bioassay of two species of freshwater microalgae, *Scenedesmus obliquus* and *Chlorella pyrenoidosa*, which can be found in tropical regions of Australia (Day et al., 1995). Furthermore, the test temperature conditions, 25 °C, were more relevant to GBR waters than what is typically used in ecotoxicity tests for temperate species (e.g. 20 or 21 °C). From the literature, the Ma (2002) study provided the most complete set of EC50 concentrations for PSII herbicides, conducted on multiple phototrophic species under the same test conditions. TEFs were derived based on the relative toxicity of diuron, ametryn, simazine and prometryn to atrazine. Atrazine was chosen to derive TEFs because the Australian and New Zealand Trigger Value (TV, ANZECC and ARMCANZ, 2000) for atrazine was of high reliability while the others were of lower reliability and because diuron (the most toxic of the measured PSII herbicides) is about to be banned in Australia. Trigger values are the numerical limits for contaminants in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000). For slightly to moderately modified waterbodies (that would apply to most catchments in agricultural areas) the TVs aim to protect 95% of species. Deriving such TVs was only possible when there were sufficient data to permit the use of the BurrliOZ species sensitivity distribution method (Campbell et al., 2000). In all other cases, the assessment factor method was used (i.e. lowest toxicity value was divided by an assessment factor); the resulting TVs do not correspond to protecting any percentage of species, but provide a generic level of protection. All TVs will henceforth be referred to simply as TVs.

2.6. Reporting pesticide concentrations

Pesticide concentrations were only reported for grab samples, passive sampler data were used for presence/absence reporting only. For presence/absence, frequency and TEQ calculations of grab samples, pesticides were only considered present when concentrations were equal to or above the limit of reporting (LOR).

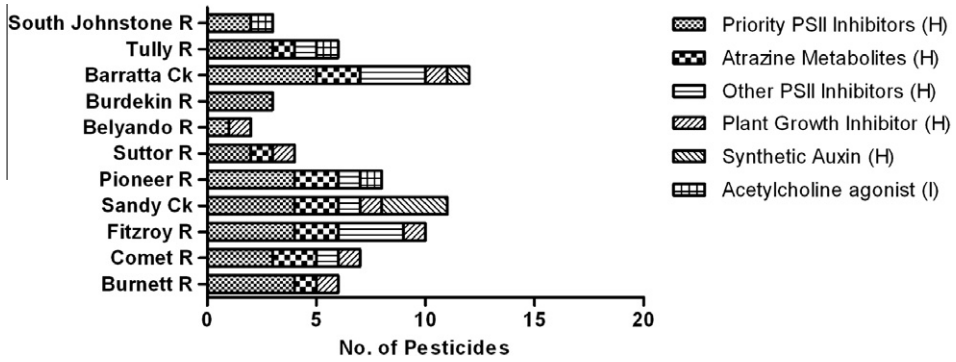

Fig. 2. Pesticide richness detected in grab samples at each site. Pesticides were grouped according to their mode of action and target organisms; H = herbicide, I = insecticide. Note that the synthetic auxins were only tested for at Barratta and Sandy creeks.

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The 95th percentiles of individual pesticide concentrations were calculated for each site and these values were compared to the appropriate TVs to determine if the TVs had been exceeded and therefore posed a potential risk. The 95th percentiles were calculated according to the following equation:

$$Cp = p \times \frac{n+1}{100}$$

where, Cp = concentration of the pth percentile, and n = the number of values in the data set (including all detections below the LOR).

Using the same methodology the 95th percentiles of the TEQ values were calculated for each site and these were compared to the atrazine TV.

3. Results

3.1. Presence/absence

The number of different pesticides detected was calculated for each site over the entire sampling period. Figs. 2 and 3 depict the total number of pesticides (grouped according to mode of action) at each site that were above the LOR, based on detections from grab and passive sampling, respectively. Barratta Creek had the greatest number of pesticides detected, but also had the greatest variety of pesticide types in both grab and passive samples. Sampling sites within the Burdekin catchment (the Burdekin, Belyando and Suttor rivers) had the least number of pesticides detected by both sampling methods and furthermore, only herbicides were detected.

In general, passive samplers detected a greater number of pesticides at each site than grab sampling (Figs. 2 and 3 and Table 2). Grab sampling (Fig. 2) detected only one type of insecticide, imidacloprid, whereas the passive samplers were able to additionally detect five OP insecticides (diazinon, chlorpyrifos, chlorfenvinphos, prothiophos and propiconazole), three OC insecticides (dieldrin, endosulfan beta and endosulfan sulphate), as well as a fungicide (tebuconazole).

One major difference noted in the two different sampling methods was the results from South Johnstone River (in the Johnstone River catchment). The grab samples detected only three different pesticides, indicating this site was one of the least contaminated sites surveyed (in terms of presence/absence). However, the results obtained from the passive samplers indicated that the South Johnstone River site had the second greatest number of pesticides present consisting of chemicals with five different modes of action.

The presence of PSII herbicides was consistent across all catchments surveyed. At least one of the five priority PSII herbicides (ametryn, atrazine, diuron, hexazinone and tebuthiuron) was detected at each site (Table 2), with all five priority PSII herbicides being detected at both Barratta Creek (Haughton River catchment) and the Fitzroy River (Fitzroy River catchment). Atrazine was detected at all sites by both sampling methods (Table 2), and at least one of its metabolites, desethyl atrazine and desisopropyl atrazine (Figs. 2 and 3), were also detected across all sites (but not consistently for both methods), demonstrating the widespread presence of atrazine. Hexazinone was also detected at all sites with passive samplers, but only seven sites with grab samples. Ametryn was detected at the least number of sites, i.e. three sites by grab samples and at five sites by passive samples, followed by diuron (eight sites for both types of samples) and tebuthiuron (seven sites for grabs and nine sites for passive samples).

Table 2
Presence/absence of the Reef Plan's (2009) five priority photosystem II herbicides at each of the monitoring sites. The presence of pesticides in each catchment was indicated by (▫) for grab samples and (▨) for passive samples.

Site	Ametryn	Atrazine	Diuron	Hexazinone	Tebuthiuron
Sth Johnstone R		▫▨	▫▨	▫▨	▨
Tully R		▫▨	▫▨	▫▨	▨
Barratta Ck	▫▨	▫▨	▫▨	▫▨	▫▨
Burdekin R		▫▨	▫▨	▫▨	▫▨
Belyando R		▫▨		▫▨	▫▨
Suttor R		▫▨		▫▨	▫▨
Pioneer R	▫▨	▫▨	▫▨	▫▨	
Sandy Ck	▫▨	▫▨	▫▨	▫▨	
Fitzroy R	▨	▫▨	▫▨	▫▨	▫▨
Comet R	▨	▫▨		▫▨	▫▨
Burnett R		▫▨	▫▨	▫▨	▫▨

3.2. Frequency of detection

In order to assess the most common pesticides entering the GBR lagoon through catchment runoff, the frequency of pesticide detection was calculated for all samples analysed. From the 268 grab samples analysed using LC–MS (Fig. 4), seven different PSII herbicides were detected, with atrazine, hexazinone and tebuthiuron the most frequently detected pesticides (occurring in more than 50% of samples). Ametryn was detected the least of the five priority PSII herbicides, being detected in less than 20% of samples. Metolachor, a plant growth inhibitor, and the insecticide, imidacloprid, were also frequently detected, occurring in approximately 30% of samples.

Thirteen samples were analysed for phenoxy acid herbicides from two sites, Barratta Creek and Sandy Creek (Fig. 4). The synthetic auxins, 2,4-D and MCPA, were detected in more than 90% and 60% of these samples (respectively). Another synthetic auxin, fluroxypyr, was also detected but in less than 10% of samples.

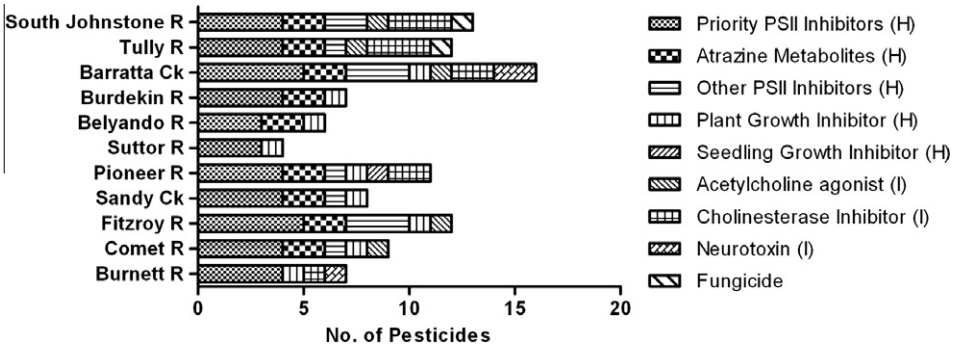

Fig. 3. Pesticide richness detected in passive samplers (ED, SPMD and PDMS) at each site. Pesticides were grouped according to their mode of action and target organisms; H = herbicide, I = insecticide.

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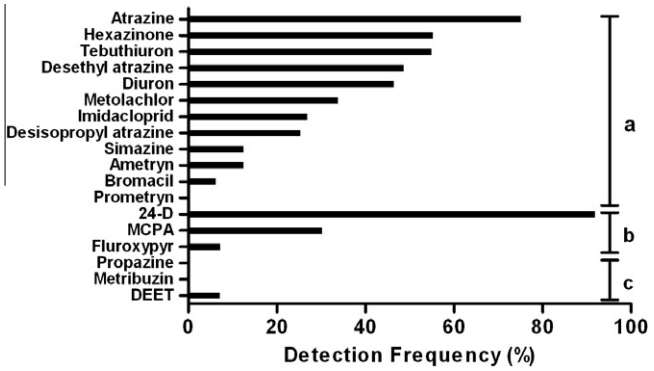

Fig. 4. Frequency of pesticides detection from grab samples collected across all sites. Frequency (%) was determined based on the number of samples that were analysed for (a) LC–MS, $n = 268$; (b) phenoxy herbicides $n = 13$; and (c) GC–MS, $n = 80$.

Samples analysed using GC–MS, which is able to detect chemicals such as OPs and OCs, only detected low frequencies (< 1%) of two herbicides, metribuzin and propazine, and DEET, an insect repellant.

3.3. Pesticide discharge characteristics

The five priority PSII herbicides were examined, along with flow data, to assess the potential exposure patterns of these herbicides on biota. Two examples of a catchment's pesticide discharge characteristics are presented here; Barratta Creek a small catchment of approximately 753 km^2 (Fig. 5), and the Fitzroy River the largest catchment sampled, with approximately 135,757 km^2 (Fig. 6).

Concentration trends at Barratta Creek (Fig. 5) demonstrated a typical first flush effect, i.e. high concentrations of pesticides (e.g. 16 $\mu g\,L^{-1}$ of atrazine, 6.5 $\mu g\,L^{-1}$ of diuron) in the first rain event of the wet season (December 2009) after which concentrations decreased as the wet season progressed interspersed with a spike in the concentrations during two events. Both pesticide concentration trends and flow trends were different for the Fitzroy River (Fig. 6) compared to Barratta Creek. Whereas the flow for Barratta Creek was composed of small, short-term events (a few days), Fitzroy River had a much larger volume of water that continued throughout the wet season. In terms of trends in pesticide discharge, concentrations in the Fitzroy River were generally lower than those reported at Barratta Creek (note the differences in scale on *y*-axis) and were less variable between events. In contrast to Barratta Creek, the pesticide trends for the Fitzroy River showed a general increase in concentration of tebuthiuron and atrazine at the start of the wet season (January and February) and then remained fairly stable for the rest of the wet season. It is important to also note that in both catchments (Figs. 5 and 6) pesticides remained present in samples throughout the wet season which lasted for two to three months.

3.4. Pesticide toxicity

Pesticide concentrations reported from grab sample monitoring were compared to the Australian and New Zealand WQG (ANZECC and ARMCANZ, 2000) TVs for the protection of aquatic ecosystems. The 95th percentile concentration was calculated for each pesticide from the distribution of samples collected at each site (Table 3). At Barratta Creek one sample could have been considered an outlier as no pesticides were detected in it, in contrast to all other samples collected from that site. Rather than omitting this potential outlier the 95th percentiles for atrazine and diuron at Barratta Creek were calculated both with and without this particular sample as these were the two chemicals where the 95th percentiles based on all the concentration data were closest to the TVs (Table 3). For both chemicals excluding the one potential outlier increased the 95th percentiles. In the case of atrazine the 95th percentile increased from 12.58 to 13.15 $\mu g\,L^{-1}$, the latter exceeding the TV. For diuron the 95th percentile increased from 5.63 to 5.78 $\mu g\,L^{-1}$ but both exceeded the TV.

Of the 18 different pesticides that were detected from grab samples, only three pesticides exceeded TVs, i.e. atrazine (refer to previous paragraph), diuron and metolachlor. Nine of the detected pesticides did not have Australian and New Zealand TVs (Table 3) and therefore no comparisons could be made for these chemicals.

Of the 11 sampling sites, eight sites had at least one pesticide above the Australian and New Zealand (ANZECC and ARMCANZ, 2000) TVs. Metolachlor was the pesticide that most frequently exceeded its TV. Barratta Creek had the highest number of pesticides (three) that exceeded TVs and was the only site in which atrazine exceeded its TV. Barratta Creek also had the highest 95th percentile concentrations of atrazine (13.15 $\mu g\,L^{-1}$) and diuron (5.78 $\mu g\,L^{-1}$), compared to other sites. For the five priority PSII herbicides, only four sites exceeded TVs.

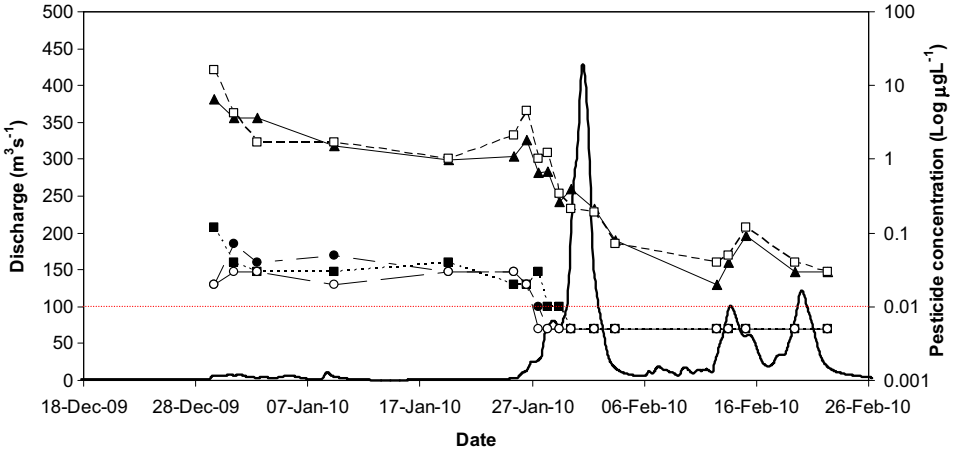

Fig. 5. Discharge ($m^3\,s^{-1}$) and pesticide concentrations ($\mu g\,L^{-1}$) for Barratta Creek during the 2009/2010 wet season. Symbols represent the five priority PSII herbicides; diuron (▲), atrazine (□), hexazinone (■), ametryn (●) and tebuthiuron (○). Solid black line represents discharge ($m^3\,s^{-1}$), red line represents the limit of reporting (LOR) ($\mu g\,L^{-1}$). Detections below the LOR were reported as half the value of the LOR. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this paper.)

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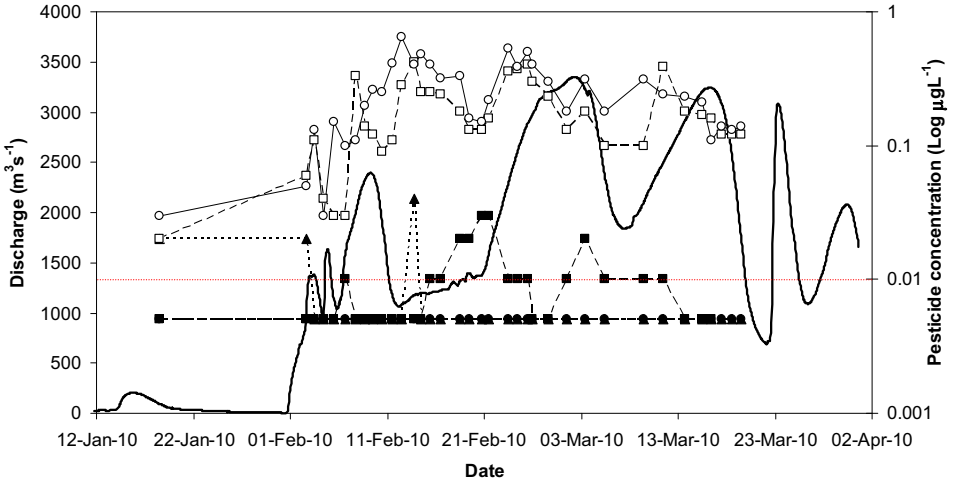

Fig. 6. Discharge ($m^3 s^{-1}$) and pesticide concentrations ($\mu g L^{-1}$) for Fitzroy River during the 2009/2010 wet season. Symbols represent the five priority PSII herbicides; diuron (▲), atrazine (□), hexazinone (■), ametryn (●) and tebuthiuron (○). Solid black line represents discharge ($m^3 s^{-1}$), red line represents the limit of reporting (LOR) ($\mu g L^{-1}$). Detection below the LOR were reported as half the value of the LOR. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this paper.)

Table 3
95th percentile pesticide concentrations calculated from 2009/2010 wet season (grab sampling only) from 11 sites within the Great Barrier Reef catchment area. Values were compared to ANZECC and ARMCANZ (2000) water quality guideline trigger values (TVs). Values in bold indicate concentrations that exceed ANZECC and ARMCANZ (2000) TVs, values in italics indicate concentrations that equal trigger values.

Pesticide	Trigger value[a] ($\mu g L^{-1}$)	Barratta Ck	Tully R	Suttor R	S. Johnstone R	Sandy Ck	Pioneer R	Burdekin R	Fitzroy R	Comet R	Burnett R	Belyando R
Ametryn	n/a	0.06	–	–	–	0.24	0.09	–	–	–	–	–
Atrazine	13	**12.58–13.15**[c]	0.32	0.20	0.03	2.58	1.90	0.03	0.40	3.10	0.08	0.02
Desethyl atrazine	n/a	0.89	0.03	0.02	–	0.18	0.27	–	0.04	0.14	0.01	–
Desisopropyl atrazine	n/a	0.28	–	–	–	0.06	0.12	–	0.03	0.06	–	–
Diuron	0.2[b]	**5.63–5.78**[c]	**0.58**	–	0.14	**4.70**	**3.40**	0.02	0.02		0.13	–
Hexazinone	75[b]	0.10	0.28	–	–	1.86	0.98	–	0.03	0.08	0.04	–
Prometryn	n/a	–	–	–	–	–	–	–	0.00	–	–	–
Simazine	3.2	0.04	0.03	–	–	0.01	0.03	–	0.02	0.04	–	–
Tebuthiuron	2.2	0.03	–	0.67	–	–	–	0.07	0.52	0.08	0.04	0.27
Bromacil	180[b]	–	–	–	–	0.03	–	–	0.02			
Metolachlor	0.02[b]	**0.05**	–	**0.42**	–	**0.05**	–	–	**0.18**	**0.31**	**0.06**	*0.02*
Imidacloprid	n/a	0.007	0.06	–	0.06	0.08	0.07	–	–	–	–	–
2,4-D	280	0.50	n/t	n/t	n/t	1.10	n/t	n/t	n/t	n/t	n/t	n/t
Fluroxypyr	n/a	–	n/t	n/t	n/t	0.20	n/t	n/t	n/t	n/t	n/t	n/t
MCPA	1.4[b]	–	n/t	n/t	n/t	0.50	n/t	n/t	n/t	n/t	n/t	n/t
Metribuzin	n/a	0.2	–	–	–	–	–	–	–	–	–	–
Propazine	n/a	0.2	–	–	–	–	–	–	–	–	–	–
DEET	n/a	–	–	–	–	–	–	–	–	0.63	–	–

n/a = Not available; n/t = not tested; dash (–) = below the limit of reporting.
[a] See Section 2 for a definition of the ANZECC and ARMCANZ (2000) TVs provided;
[b] Low reliability trigger value, i.e. an interim or indicative working level only due to the absence of a data set of sufficient quantity to derive the trigger value.
[c] Two 95th percentile values were calculated, refer to Section 3.4 for explanation.

To derive an estimation of the toxicity of PSII herbicides as a mixture, the 95th percentile for TEQ_{SO} (toxic equivalent quotient for *S. obliquus*) and TEQ_{CP} (toxic equivalent quotient for *C. pyrenoidosa*) were calculated for each site (Table 4). Atrazine equivalent concentrations far exceeded the detected atrazine concentrations, as would be expected, with the calculated 95th percentile TEQ concentration being more than 100 times the detected atrazine concentration for a number of sites. The highest atrazine equivalent concentration detected was 807 $\mu g L^{-1}$ at Barratta Creek (data not shown) with 672.3 $\mu g L^{-1}$ as the 95th percentile concentration (TEQ_{CP}). Such high atrazine equivalent concentrations for these samples at Barratta Creek were principally derived from the high diuron concentrations which accounted for 97% of the mixture toxicity (data not shown).

The number of sites that exceeded the atrazine TV (13 $\mu g L^{-1}$) increased to six for TEQ_{CP}, and remained at four for TEQ_{SO} (Table 4). The number of events where TEQ_{SO} and TEQ_{CP} exceeded the atrazine TV and which atrazine and diuron exceeded TVs on their own was recorded in Table 5. The number of events that exceeded TVs was greater for four sites (Barratta Creek, South Johnstone River, Sandy Creek and Burnett River) when PSII herbicide concentrations were combined using TEQ_{CP} compared to atrazine or diuron concentrations on their own. On the other hand, at two sites (Tully River and Sandy Creek), the number of events that exceeded TVs using TEQ_{SO} was less than the number of events in which diuron concentrations exceeded the TVs. When TEQ concentrations were graphed over time (days), the duration of atrazine TV exceedances was demonstrated (Figs. 7 and 8). At Barratta Creek, the atrazine TV was exceeded for approximately 30 consecutive days when calculated with both TEQ_{SO} and TEQ_{CP}. At Sandy Creek TEQ_{CP} and TEQ_{SO} were above the atrazine TV for more than 30 and 18 consecutive days (data not shown). For the Pioneer and Tully rivers,

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Table 4
The 95th percentile of atrazine toxic equivalent (TEQ) concentrations calculated from the toxic equivalency factors (TEFs) of the PSII herbicides; atrazine, diuron, ametryn, simazine and prometryn. Atrazine TEQs were determined from Ma (2002) for the freshwater microalgal species, *Scenedesmus obliquus* (TEQ_{SO}) and *Chlorella pyrenoidosa* (TEQ_{CP}). Values are compared to the ANZECC and ARMCANZ (2000) trigger value (TV) for atrazine.

Site	TEQ_{SO} (μg L^{-1})	TEQ_{CP} (μg L^{-1})
Barratta Ck	**186.6**	**672.3**
Tully R	**19.14**	**69.7**
Suttor R	0.23	0.23
Sth Johnstone R	4.58	**16.83**
Sandy Ck	**157.4**	**664.0**
Pioneer R	**112.6**	**438.0**
Burdekin R	0.59	2.16
Fitzroy R	0.71	2.46
Comet R	3.11	3.15
Burnett R	4.33	**15.7**
Belyando R	0.02	0.02
Atrazine trigger value[a]	13	13

[a] See Section 2 for a definition of the ANZECC and ARMCANZ (2000) TVs provided.

concentrations of TEQ_{CP} and TEQ_{SO} above the atrazine TV were of shorter duration, up to eight and two consecutive days (respectively). Although atrazine TV exceedances were short-term at Tully, there were pulses of high concentrations (i.e. >13 μg L^{-1}) for multiple events (Fig. 8).

4. Discussion

The results from this study are in agreement with the scientific consensus (Brodie et al., 2008) that there is a widespread problem of pesticide contamination in catchments draining into the GBR. Although the Reef Plan (2009) pesticide monitoring program is in its early stages, the data collected thus far is already providing valuable information on the extent of the pesticide contamination in the GBR catchments, and the potential threat it poses to biota.

The contamination was prevalent on both a spatial and temporal scale with pesticide detections recorded at all 11 sites (i.e. across eight catchments) throughout the 2009–2010 wet season. However, the extent of contamination extended further than just their presence on a temporal and spatial scale. The degree of contamination was truly realised in the number of different pesticides that were recorded at each site, the classes of pesticides that were detected, the commonality of mixtures in a sample, and the concentrations that were present.

Between 2 and 16 different pesticides were recorded at each site, with PSII herbicides detected at all sites (Figs. 2 and 3). The PSII herbicides were the most frequently detected pesticides across all eight catchments (Figs. 2 and 3), occurring in up to 80% of samples (Fig. 4). This result was not surprising based on the recurrent reporting of the presence of PSII herbicides in the GBR lagoon and GBR catchments (e.g. Lewis et al., 2009; Davis et al., 2008; Packett et al., 2009; Shaw and Müller, 2005). Each of the Reef Plan's (2009) five priority PSII herbicides were detected (Table 2) as well as other PSII herbicides, i.e. simazine, bromacil, propazine, prometryn and metribuzin. The five priority pesticides were not equally spread throughout the GBRCA; diuron, ametryn and tebuthiuron were confined to particular catchments, whereas atrazine and hexazinone were present at every site (Table 2). Barratta Creek and Fitzroy River were 'hot spots' for the priority PSII herbicides, with all five detected. It was also found that PSII herbicides were often detected together in a sample; for example, individual samples from Barratta Creek were composed of up to seven PSII herbicides (data not shown for individual samples). Along with the PSII inhibitors, other types of pesticides known to exhibit toxic effects on aquatic biota were detected including other classes of herbicides, insecticides and a fungicide.

The herbicides (other than PSII herbicides) detected included metolachlor, a plant growth inhibitor, which was recorded at nine sites (Fig. 3) in more than 30% of samples (Fig. 4). Metolachlor has been shown to be toxic to aquatic organisms, impacting the growth of phototrophs such as microalgae and macrophytes (Fairchild et al., 1998). The degradation products of atrazine, desethyl atrazine and desisopropyl atrazine, were also frequently detected at most sites. Additionally, the phenoxy acid herbicide 2,4-D was detected in over 90% of samples ($n = 13$) while MCPA and fluroxypyr were detected regularly (10–30% of samples) at the two sites they were monitored – Barratta and Sandy Creeks (Fig. 4). As previously discussed, herbicides pose a real threat to aquatic phototrophs which play a key role in freshwater, estuarine and coastal marine ecosystems, providing vital services to the GBR, such as nutrient cycling, food resources and habitats (Schaffelke et al., 2005; Waycott et al., 2007).

Insecticides (OPs, OCs and an acetylcholine agonist) were also detected across the majority of the monitoring sites. Over the 2009–2010 wet season, the presence of the acetylcholine agonist, imidacloprid, was widespread, occurring in six of the eleven sites: Barratta Creek and the Comet, Johnstone, Tully, Pioneer and Fitzroy rivers (Figs. 2 and 3). Imidacloprid was detected in more than 20% of grab samples (Fig. 4) as well as passive samplers and has been shown to be toxic to aquatic invertebrates (Stoughton et al., 2008). The organophosphate and organochlorine insecticides were only detected with passive samplers and therefore only presence/absence data were available. Organophosphates were detected at

Table 5
Number of events in which the 95th percentile concentration for atrazine, diuron, TEQ_{SO} and TEQ_{CP}, exceeded ANZECC and ARMCANZ (2000) TVs.

Site	Total no. of events sampled	No. of events exceeding trigger values[a]			
		Atrazine	DCMU	TEQ_{SO}	TEQ_{CP}
Barratta Ck	6	1	2	2	3
Tully R	6	0	3	2	3
Suttor R	3	0	0	0	0
Sth Johnstone R	4	0	0	0	1
Sandy Ck	7	0	6	4	7
Pioneer R	2	0	2	2	2
Burdekin R	1	0	0	0	0
Fitzroy R	5	0	0	0	0
Comet R	3	0	0	0	0
Burnett R	1	0	0	0	1
Belyando R	3	0	0	0	0
Trigger value[a] (μg L^{-1})	–	13	0.2	13	13

[a] See Section 2 for a definition of the ANZECC and ARMCANZ (2000) trigger values provided.

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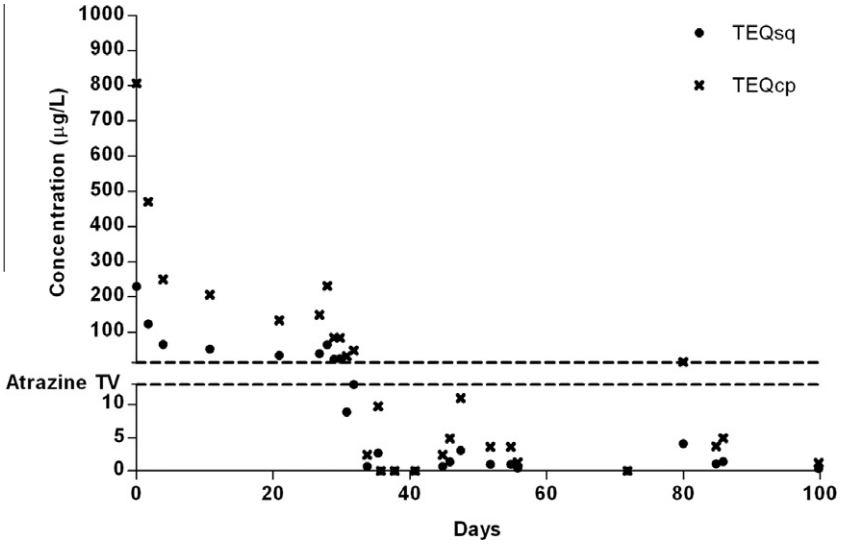

Fig. 7. Atrazine toxic equivalent quotients (TEQs) for the freshwater microalgal species, *Scenedesmus obliquus* (TEQ_{SO}) and *Chlorella pyrenoidosa* (TEQ_{CP}) at Barratta Creek over the 2009–2010 wet season. Time (days) was calculated from the date the first sample was collected. Dotted line indicates the atrazine trigger value for 95% protection of species (13 µg L^{-1}). Note that the scale changes on the *y*-axis after the segment break.

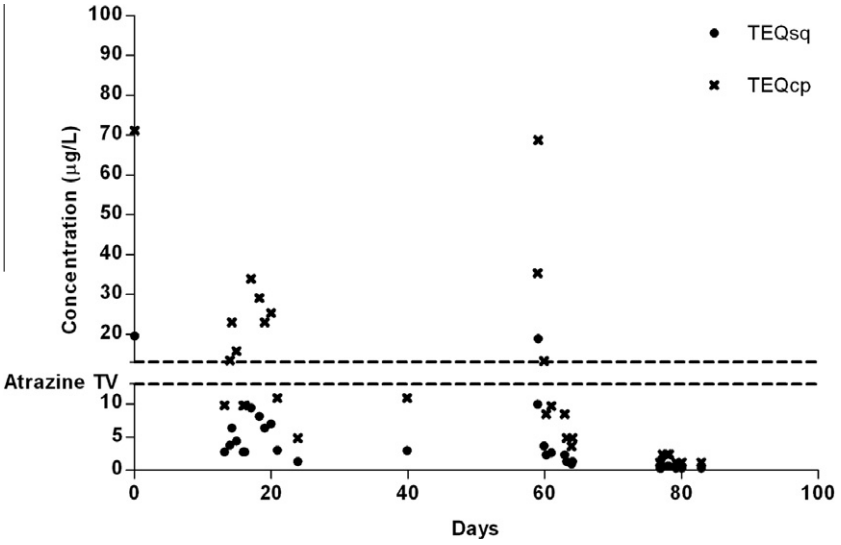

Fig. 8. Atrazine toxic equivalent quotients (TEQs) for the freshwater microalgal species, *Scenedesmus obliquus* (TEQ_{SO}) and *Chlorella pyrenoidosa* (TEQ_{CP}) at Tully River over the 2009–2010 wet season. Time (days) was calculated from the date the first sample was collected. Dotted line indicates the atrazine trigger value for 95% protection of species (13 µg L^{-1}). Note that the scale changes on the *y*-axis after the segment break.

five sites (cholinesterase inhibitors in Fig. 3) and OCs, including the recently banned endosulfan, were detected at two sites (neurotoxins in Fig. 3). The presence of OPs and OCs in catchments draining into the GBR is of concern due to their ability to bioaccumulate, their persistence in aquatic environments and their endocrine disrupting properties (Mortimer, 2000; Kojima et al., 2004).

The threat to aquatic biota from individual pesticides was assessed by comparing concentration data (grab samples only) to the Australian and New Zealand TVs (ANZECC and ARMCANZ, 2000). As recommended by the Australian and New Zealand WQGs (ANZECC and ARMCANZ, 2000) if the 95th percentile of concentrations exceed the TV for a chemical at a site, then there is a moderate to high probability of toxicological effects occurring and further investigation is warranted to determine the potential risk of that chemical to the biota in that ecosystem. In this study, exceedances of the TV occurred at eight sites by three different chemicals: atrazine, diuron and metolachlor (Table 3). However, this assessment may in fact be an underestimation as no TVs were available for nine of the detected pesticides. Of those that did have a TV for comparison, only half of these again had values that were of high reliability. This is a crucial knowledge gap that should be addressed in order to permit a more comprehensive and reliable estimate of the hazard posed by pesticides.

When PSII herbicides were combined using the TEQ approach the toxicity of samples was far greater than the toxicity of the pesticides on their own (compare values in Tables 3 and 4). For example, the 95th percentiles of atrazine TEQ_{CP} at Barratta Creek (the site with the highest pesticide contamination) were approximately 50 times larger than the atrazine TV (Table 4), compared to being approximately equal for atrazine acting individually (Table 3). Furthermore, atrazine TEQs exceeded the Australian and New Zealand TVs (ANZECC and ARMCANZ, 2000) at more sites and more often when compared to the exceedances of the individual chemicals (Table 5).

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The mixtures observed in samples were not just restricted to PSII herbicides. The grab samples often consisted of multiple herbicide classes as well as the insecticide imidacloprid. Additionally, the passive samplers adsorbed an even greater number of chemicals during their deployment. The presence of such complex mixtures with chemicals having different modes of action would provide opportunity for interactive effects (including synergism and antagonism) on biota. For instance, it has been demonstrated that atrazine in combination with its metabolites can produce additive and synergistic effects on phototrophic microorganisms (Stratton, 1984). In addition, there is evidence that, when in combination, atrazine and organophosphates (e.g. chlorpyrifos) can produce synergistic effects (Pape-Lindstrom and Lydy, 1997). However, determining the toxicity of a complex mixture consisting of chemicals with many modes of action becomes difficult to derive without conducting whole effluent toxicity tests.

The TEQ results demonstrate the severe underestimation of the true toxicity of a sample if mixtures are not taken into consideration. Even the TEQ concentrations reported here are likely to be an underestimation of toxicity, as only half of the PSII herbicides that were detected in the GBR catchments were accounted for, and the herbicides, insecticides and fungicide with a different mode of action were not included in the TEQ calculations. Furthermore, to be more accurate in using the toxic equivalency approach for GBR catchments, a greater number of species from different trophic orders representative of the GBR catchments should be used to derive TEFs.

There is also debate as to how representative the Australian and New Zealand WQGs (ANZECC and ARMCANZ, 2000) are for tropical species (van Dam et al., 2008) and this was one reason for deriving Water Quality Guidelines for the Great Barrier Reef (Great Barrier Reef Marine Park Authority, 2008). The current Australian and New Zealand WQGs (ANZECC and ARMCANZ, 2000) are predominantly derived from temperate and cool-temperate species, which have been proven to vary in sensitivity to tropical species (Kwok et al., 2007). The results, though, do highlight a pressing need for further investigations of the risk to biota in the catchments monitored in this study.

The potential risks to biota may be further exacerbated by the nature of the exposure patterns. Some catchments showed that highly variable, first flush and pulsed exposure characteristics would be likely to occur, e.g. Barratta Creek and Tully River (Figs. 5 and 8). Whereas other catchments showed that a more low level, chronic exposure would be likely, e.g. Fitzroy River (Fig. 6). Again when assessing the TEQ results, biota were potentially exposed at Barratta Creek and the Tully River, to concentrations greater than the TVs for up to 30 days and to low level concentrations for more than 70 days (Figs. 7 and 8).

PSII herbicides may cause damage or stress to phototrophs in either of two ways. Firstly, high concentrations of PSII herbicides with relatively high light levels can lead to photoinhibition and the formation of reactive oxygen species causing protein damage (Beligni and Lamattina, 2002; Fufezan et al., 2002). In this instance, damage will occur in the short-term, but if exposure was long term this type of damage can become irreparable (Falkowski et al., 2007). Secondly, the impact of PSII herbicides on the photosynthetic apparatus occurs together with shading caused by high total suspended solids concentrations (Haynes and Michalek-Wagner, 2000) that may reduce the phototroph's ability to produce carbohydrates. Reduced electron transport due to PSII binding and shading will ultimately lead to stress and reduced growth in the organism if these conditions are sustained for long periods of time (Harrington et al., 2005).

The second scenario involves the occurrence of multiple stressors in flood plumes, a circumstance that needs to be taken into account when assessing the impact of pesticides on GBR biota. For instance, high concentrations of sediment and suspended solids are ubiquitous with the freshwater flood plumes entering the GBR lagoon (Devlin et al., 2001; Furnas, 2003). Large sediment loads from flood plumes have previously been linked with impacts to seagrasses (Preen et al., 1995; Longstaff and Dennison, 1999). Furthermore, a synergistic interaction between sediment and a PSII inhibitor to coralline algae has been reported (Harrington et al., 2005).

The impact of pesticides to biota in these catchments is likely to have been occurring for many years. PSII herbicides were detected in the mouths of the Tully and Johnstone Rivers in 2004 and 2005 (Shaw et al., 2010). Similarly to this study, diuron concentrations in samples collected at Sandy Creek and Pioneer River were reported to exceed Australian and New Zealand TVs (ANZECC and ARMCANZ, 2000) in 2002 (Mitchell et al., 2005). Monitoring conducted between 2005 and 2008 in the Burdekin and Haughton catchments reported diuron and atrazine in exceedance of the Australian and New Zealand (ANZECC and ARMCANZ, 2000) TVs. Metolachlor was also previously recorded to have exceeded its TV in the Burdekin-Townsville region (Davis et al., 2008; Lewis et al., 2009). Diuron was found in sediments of subtidal regions of the Johnstone and Fitzroy rivers in 1997, in addition to lindane, dieldrin and DDE in the Johnstone River and DDE in the Fitroy and Burdekin rivers (Haynes et al., 2000). Additionally, insecticides such as OPs, OCs and ACh agonists have previously been detected in the Haughton, Burdekin and Fitzroy catchments (Davis et al., 2008; Lewis et al., 2009; Packett et al., 2009).

It is also likely that the extent of pesticide contamination covers a large area over the GBRCA, particularly if the very reasonable assumption is made that other catchments with agricultural land use are also transporting pesticides. Large-scale contamination could pose major problems for reef communities in their ability to recover from natural disturbances such as cyclones, bleaching events or crown-of-thorns starfish (Nyström et al., 2000).

5. Conclusions

This study has found that there is widespread pesticide contamination across the GBR catchments that discharge to the GBR lagoon. The contamination is characterised by frequent and widespread occurrences of pesticides including PSII herbicides and the presence of complex pesticide mixtures. Concentrations of individual pesticides and mixtures of PSII herbicides exceeded the Australian and New Zealand TVs (ANZECC and ARMCANZ, 2000) at a number of sites in the 2009–2010 wet season. These exceedances and the potential transport of these pesticides into the GBR lagoon are concerning for the health and resilience of the reef. The evaluation of potential environmental harm was not fully characterised due a lack of high reliability TVs and toxic equivalence factors. In addition, ecotoxicological research of tropical species representative of north Queensland aquatic ecosystems needs to be thoroughly examined, such that laboratory bioassays can be conducted to indicate the toxicity of End of System waters sampled from rivers transporting agricultural runoff. Bioassays of this nature would provide insight into the concomitant effects of multiple stressors to tropical freshwater, estuarine and marine systems.

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